DESIGN, SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL MATERIALS

Synopsis

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I. Introduction

Functional materials are defined as novel chemical substances comprising functional organic and /or inorganic fragment(s) competent of portraying predestined properties. [1] Indubitably, they constitute an important class of materials facilitating in-depth basic research and advanced cutting-edge technology developments. They have become the quintessential substances of the modern generation. Although a broad range of substances fall under this category, some of the well-known, highly promising and performing materials include thermotropic [2] and lyotropic liquid crystals (LCs), [3] metallomesogens, [4] organogels, [5] biomaterials, [6] metal-ligand coordination polymers (COPs), [7] metal-organic frameworks (MOFs), [8] covalent organic frameworks (COFs), [9] nanomaterials, [10]metallic oxides, [11]soft-nano composites, [12]conducting polymers, [13]organic-inorganic hybrid semiconductors, [14] etc. Given the fact that their chemical and physical characteristics are highly sensitive to the external stimuli such as light, sound, temperature, pressure, magnetic field, electric field, sonic field, pH value etc., they have been serving as the active media in a wide range of advanced scientific and technological endeavours. [1] In particular, they hold significant potential and value in biomedicine/healthcare, electronics, display device technology, chemical sensing, fluorescence, photonics, transduction, ferroics, piezo and pyroelectrics, superconductors, automotive industries, energy conversion & storage, etc. [1]

The usage of functional materials in fabricating high-demand products, such as, say from flexible displays to radio-frequency detector appears to be appropriate and highly rewarding. Therefore, during the last few decades, they have been investigated for their fitability and actual-performance test in devices such as field effect transistors (FETs), solar photovoltaics (PVs), organic light emitting diodes (OLEDs), sensors etc. [1-14] However, the experimental results accumulated hitherto seem to be inadequate especially in terms of appropriate material design and realization. Thus, the quest for creation of new materials and understanding their structure-property correlations continues intensively. Needless to say, such research endeavours involving the strategic design, synthesis characterization of completely new technological materials are absolutely essential. Inspired by these observations, we have focussed our attention on the molecular design and synthesis of technologically important thermotropic LCs and COPs. We have largely worked on LCs covering both conventional and nonconventional mesomorphic

compounds and to some extent on COPs. In the following sections the general aspects of these functional materials are discussed.

I. Liquid crystals

Liquid crystal (LC) phases which are birefringent fluids constitute yet another state of matter. They are thermodynamically located between the crystalline solid and the isotropic liquid states. Hitherto, a wide variety of LC phases have been discovered that essentially possess orientation order, and some of them possess positional order additionally. They have been attracting a great deal of attention due to their huge promise in fundamental research and applied science.

I.1. Classification of liquid crystals

Liquid crystals are generally classified into two categories, namely lyotropic and thermotropic LCs. Lyotropic liquid crystals are obtained by the action of solvent on amphiphilic/amphotropic substances, whereas thermotropic LCs are obtained by the action of heat on shape anisotropic organic or metal containing organic molecules called mesogens or LCs. Thermodynamically stable mesophases which appear both on heating and cooling are termed enantiotropic, while the thermotropic mesophases that appear only on the cooling process (below the melting temperature of the mesogens) are monotropic.

I.1A. Lyotropic liquid crystals

Lyotropic LCs are generally formed by the self-assembly of amphiphilic/amphotropic molecules in a solvent medium (usually water) under the appropriate conditions such as temperature and concentration. Lyotropic LCs are the essential components of all the living beings. A well-known biological example for lyotropic LCs is lipid bilayers of cell membranes.

I.1B. Thermotropic liquid crystals

Thermotropic LCs exhibit mesomorphism when they are heated above their melting point. The mesomorphism is generally observed in shape anisotropic organic or metal-containing organic materials comprising rigid core(s) and flexible tail(s). The presence of flexible tails accounts for the fluidity (mobility) whereas the rigid entity of the mesogens render the partial

order (orientational/positional order) to the LC phase. Although a large variety of organic compounds possess both rigid (hard) and flexible (fluid) entities, the mesomorphism is seen in only small fraction of such materials. Wherein these incompatible entities are covalently linked so as to provide shape anisotropy to the molecules. The temperature at which the transition from Crystal(Cr)-Mesophase(M) occurs is termed as the melting point whereas the temperature at which the mesophae transforms into isotropic state due to heating is called clearing temperature or point. The other important driving force for the formation for the LC phases are reduced symmetry /chirality, microphase segregation and self-organization/assembly.

I.1.1. Classification of thermotropic liquid crystals

Thermotropic LCs have been classified into different categories based on the various aspects viz., anisotropic shape, molecular size/mass, mesophase type etc. Among these the classification based on the anisotropic shape of mesogens has been adopted widely. Accordingly there are three main types of thermotropic LCs viz., rod-like LCs (calamitics), disk like LCs (discotics) and bent core (banana shaped) LCs. These LCs have been further classified into two categories: Conventional and non-conventional LCs.

I.1.1A. Conventional liquid crystals

The calamitic and discotic compounds are the classical examples of conventional LCs. The combination of rigid and flexible entities leading to an axially elongated molecular shape yields rod-like LCs (calamitics). It was believed for a long time that only the rod-like LCs exhibit mesomorphism. This assumption was disproved in 1977 by Chandrasekhar and co-workers by demonstrating that the mesogens having disk-like shape exhibit mesomorphic behaviour.[15] The disk-like LCs are formed by attaching three to several paraffin tails around a central rigid core. The spontaneous self-assemble of such conventional mesogens leads to the formation of a least ordered LC phase called the nematic (N) phase where the parallel arrangement with long range orientational order of the constituent mesogens persists; on the other hand, their self-assembly leading to microphase segregation of incompatible regions yields smectic (Sm) or columnar (Col) phase.

Such rod-like and disk-shaped mesogens possessing molecular chirality are referred to as chiral LCs. They self-assemble to yield LC chiral bulk aggregates such as helical structures of

the chiral nematic (N*) or chiral smectic C (SmC*) phases as well as layered phase the smectic A (SmA) phase; in addition they form highly frustrated LC phases such as blue phases (BPs), and twist grain boundary (TGB) phases. Such chiral phases can also be realized by the addition of guest chiral additiveto the host achiral LC phases.

I.1.1B. Non-conventional liquid crystals

The mesomorphic compounds deviating in their anisotropic shape from those of conventional LCs are generally referred to as nonconventional LCs. They have been attracting a great deal of attention not only because they display remarkable LC behaviour but also have the ability to serve as an active media in many practical applications. [2e,16] Supramolecular (self-complementing) LCs, which vary from the small to large size and even giant-size also come under this category; notably, in the mesophases formed by such substances, the mesogens interact with each other through secondary interactions such as hydrogen (H)- bonds, π–π stacking, van der Waals forces etc. [17, 18a] Some of the important examples of non-conventional systems are oligomers, [18b] polycatenars, [18c]bent-cores,[18d] polyhydroxy amphiphiles, [18e] dendrimers etc. [18f]

In view of afore mentioned interesting aspects, we intend to work on chiral LCs encompassing both conventional and nonconventional LCs.

I.2. Coordination polymers

Coordination polymers (COPs) are novel hybrid materials formed by the combination of metal ions and organic ligands. Most importantly, they can be designed such that they self-assemble to generate 1D or 2D or 3D structures where secondary interactions such as H-bonding, π-π stacking and van der Waals interactions play a vital role. They can also be made to absorb or emit light by the appropriate choice of organic ligand and/or metal ions. [19-21] They have been attracting a great deal of attention due to their high surface area, perpetual porosity, tunable optical properties, strong adsorption affinity, stable magnetic properties, etc. COPs have been utilized in the fields of gas storage,[22] heterogeneous catalysis,[23] chemical sensing,[24] energy conversion,[25] drug delivery,[26] and bioimaging etc.[27] However, the COPs capable of emitting light have been employed for the detection of various chemical species which includes the high energy materials (HEMs). [28-32] In recent times, the detection of explosives has become a tough

task for security providers, law enforcement personalities and armed forces. The usage of explosives, especially the nitro aromatics has created serious human health concerns such as anaemia, carcinogenicity, abnormal liver function, cataract development and skin irritation, etc.[33,34] Therefore, the rapid detection of such materials is essential to protect public health and environment. Many explosive sensing methods/devices/techniques have been developed which include ion mobility spectrometers,[35]colorimetric kits, fluorescence detectors, mass spectrometry,[36] electrochemical methods[37] etc. However, these methods of sensing HEMs are generally expensive, cumbersome, faulty and non-user friendly. In this context, the sensing of HEMs by using the solutions of fluorophores appears to be one of the inexpensive and hassle-free methods where the selectivity and sensitivity aspects can be addressed efficiently. Hence, we became interested in studying such fluorophoric COPs.

Scope and outlook of the thesis

It is immediately apparent from the above discussion that functional materials are promising from the viewpoints of both fundamental research and applied science. Therefore, we intended to work on such functional materials encompassing conventional LCs, nonconventional LCs and coordination polymers (COPs). In particular, we aimed to work on rod-like conventional LCs as well as nonconventional LCs which include cholesterol-based LC dimers and polycatenars. Besides we also conceived an idea of designing and synthesizing inexpensive fluorescence materials in the form of COPs capable of detecting the explosives with high sensitivity and selectivity.

Calamitic liquid crystals are in lime light due to their usage in liquid crystal displays (LCDs) which are used in various devises such as watches, phones, televisions, laptop, desktop monitors etc. In particular a simple LC phase namely, the nematic phase serves as an active (electrically responsive) media in LCDs. Likewise the chiral mesophases such as chiral nematic (N*) and chiral smectic C (SmC*) phases have been respectively used in the fabrication of thermal (temperature) sensors and ferroelectric LCDs (FLCDs). [38] However, it is important to note here that the FLCDs derived from the ferroelectric SmC* phase have added advantages.[38c] For example, FLCDs feature high resolution, wide viewing angle, high quality images,fast response time, etc. [38d] In the SmC* phase, the macroscopic helical arrangement of the constituent mesogenic molecules persists spontaneously. The helical structure exists as a result of gradual

change in the molecular tilt direction (director ***n***) from one layer to another, about an axis normal to the layer plane. In the ferroelectric SmC* phase the spontaneous polarization (P_s) originating from the special structure mentioned above formed as a consequence of the self-assembly of the chiral rod-like mesogens can be reorganised/reoriented by the application of an electrical field or by surface anchoring. Due to the presence of chiral mesogens, the local symmetry of the structure reduces to a two-fold axis of rotation leading to an in-equivalance in dipole moment along the C_2 axis perpendicular to the tilt direction. This gives rise to spontaneous polarization (P_s) in each layer. On a macroscopic level, however, there is no net polarization because the helix averages out the spontaneous polarization to zero. However, a macroscopic polarization can be achieved by unwinding the helix by the application of an electric field or shear. The application of such external forces enables the bulk SmC* phase becoming ferroelectric where the helical structure is deformed.[38e]

The end-usage of FLC mixtures as an active media for the expected device performance largely depends on availability of apt single component materials. [38f]They should, in the first place, display the SmC* phase over a wide thermal range (well below and above the room temperature) with high magnitude of spontaneous polarization (P_s). Although a wide range of FLC mixtures have been designed and prepared, there are only a few mixtures that are suitable for the fabrication of FLC mixtures. It is important to note here that the suitability of FLC mixture in the devices largely depends on the predestined vital properties of the individual (single components) constituting the mixture.[39,40]Thus, in order to provide genuine single component FLC materials showing the optimum/requisite physical characteristics, there is an absolute need of rational design and synthesis of new materials.

Among a wide variety of non-conventional LCs reported hitherto, LC dimers, which are the first members of oligomeric LCs, have been drawing wider attention due to their ability to act as model compounds for LC polymers and their remarkable phase transitional behaviour, which differs from that of the corresponding monomeric LCs.[41]The dimers formed by two identical mesogenic segments interlinked covalently via a flexible spacer of varying length and parity are called symmetric dimers; nonsymmetric dimers are formed when two non-identical (chemically dissimilar) mesogenic units are linked through a central spacer. [41f] Generally, the mesomorphic properties of this class of soft materials critically depend on the parity of the spacer. [41g]The

dimers comprising an even-parity spacer attain a rod-like shape in their all-*trans* conformation, whereas the dimers with an odd-numbered central spacer gain bent-shape where the two mesogenic entities are inclined with respect to one another. Due to the bent-shape, the odd-membered dimers possess low clearing temperature when compared to their even-member counterparts. While the symmetrical dimers serve as model compounds for LC polymers, the nonsymmetric dimers have shown rich and intriguing mesomorphism.[41-43] This is especially remarkable in the case of cholesterol-based (chiral) nonsymmetric dimers formed by linking cholesterol with another calamitic (aromatic/aromatic-alicyclic)core via a flexible spacer of varying length and parity. [44]These dimers display unprecedented LC phase sequences, re-entrant behavior, variety of frustrated phases, and technically relevant mesophases over a wide temperature range. The properties of such LC dimers, needless to say, largely depends on the length and parity of the spacer, terminal substituent(s), lateral substituents, the type of linking groups and the chemical nature of the calamitic core. Although a wide range of cholesterol-based LC dimers have been reported hitherto, the revelation of their structure-property correlation still remains elusive. Therefore, there is an absolute need and huge scope for the rational design, synthesis and characterization of new LC dimers derived from cholesterol.

Phasmidics or polycatenars are a special class of thermotropic LCs bridging the gap between conventional rod-like and disk-shaped LC molecular architectures and thus, they exhibit a rich polymesomorphism. They comprise a long rod-like core ending on either side with lipophilic segments comprising two or three flexible tails.[45-59] They have been categorized according to the total number of *n*-alkoxy tails they possess; for example, polycatenars substituted with four, five and six terminal paraffinic tails have been respectively referred to as tetracatenars, pentacatenars and hexacatenars. [46-49] That is, experimentally it has been evidenced that these hybrid mesogens not only show the nematic (N), smectic (lamellar) as well as bicontinuous/micellar cubic, tetragonal and orthorhombic three-dimensional phases but also stabilize a unique Col_h phase in a series of compounds or in a pure material. [56-60] However, such phase transitional behaviour largely depends on the number of alkoxy tails they possess on the either side of the central calamitic core. Of the variety of polycatenar LCs reported hitherto, the hexacatenars (phasmids) have been attracting attention not only because of their inherent ability to self-assemble in to the Col phase but also, they provide the opportunity to incorporate

functional characteristics through the selection of predetermined molecular structural segments. Thus, a wide variety of functional phasmids have been realized which include heterocycles, [50-55] metallomesogens, [56] ionic LCs, [57-58] photo-responsive mesogens, [59a] intra-molecular H-bonded systems, [59b,c] thermochromic LCs, [60] bent-core compounds, [61] fluorescent materials etc. [62]

However, the fluorescent phasmidic LCs, owing to their technological relevance, have been investigated intensively through the rational design and synthesis of diverse series of materials derived from functional fluorophores. [63-79] Of these, there has been a thought-provoking work by Park and co-workers reporting that phasmidic LCs, possessing intra-molecular proton-transfer (ESIPT) activity, form tilted (*J*-type) stacking in the column of the LC phases; interestingly, this assembly augments the fluorescence emission of the mesophase with a quantum yield of 34% and a large Stokes' shift (173 nm). [79]It is speculated that the ESIPT fluorescence coupled with Col behaviour make the phasmidics ideal candidates for applications in emissive LCDs, polarized organic lasers and anisotropic OLEDs. [51-79]Surprisingly, despite such attractive features, there are hardly any attempts/exploration in this direction and hence, new investigations involving the rational design, synthesis and characterization of ESIPT Col LCs, have to be undertaken rigorously.

Among the wide varieties of COPs reported thus far, luminescent COPs have recently gained enormous attention owing to their ability to act as the ideal and inexpensive sensors. [80]They are sensitive and selective materials, and thus they respond well to the additives (quenchers) which can be identified using optical signal/data.[81] The COPs derived from lanthanide metal ions are especially noteworthy. [82] In particular, the lanthanide COPs possessing self-complementing (H-bonding) organic linkers (ligands) have been successfully used for recognizing a wide range of chemical substances/species. [83]

On the other hand, the nitro aromatics, which fall under the category of high energy materials (HEMs) have been extensively used as explosive materials. Given their toxicity induced adverse effect on human health and environment, their detection has become one of the important tasks to the security persons.[84] However the ultra-sensitive detection of such explosives in their vapour phase is a difficult task because of their low volatility at ambient temperature. [85] Thus, the detection of HEMs either in their solid or solution states has been

accepted as the simple and reliable technique. In particular, the usage of solution of fluorophores for the detection of HEMs appears to be the highly promising technique where the fluorescence quenching takes place due to the interaction between electron rich (sensors) and electron deficient HEMs. However, the literature survey on this topic suggests that the investigations reported in this direction are inadequate for drawing clear conclusions of structure-property correlations. Obviously, there is need for the synthesis and characterization of different COPs derived from trivalent metallic centres.

Thus, the work presented in this thesis, entitled "**Design, Synthesis and Characterization of Functional Materials**" deals with the rational molecular design, synthesis and characterization of functional materials such as thermotropic LCs and COPs. The thesis has been divided into five Chapters (**I-V**). Chapter-I covers the fundamental aspects and applications of thermotropic LCs and COPs. The other Chapters-II, III, IV and V portray the work carried out during the doctoral study. These chapters begin with a relevant preamble of the topic, followed by the work description, and details of experimental-characterization techniques and terminate with the appropriate/important references. The work carried out under the heading of thermotropic LCs, which constitutes the major portion of the thesis (Chapters II-IV), encompasses both conventional (chiral rod-like) mesogens and non-conventional LCs (chiral LC dimers and hexacatenars). Under the section of COPs (Chapter-V), the complexes prepared using different lanthanide metal ions and an organic (tetramine) ligand have been presented.

Chapter I: Introduction to liquid crystals and their applications

This Chapter introduces the readers to functional materials, and the contents of which are mostly concerned with liquid crystals (LCs). Importantly, this portion of the thesis justifies the research work carried on LCs and coordination polymers (COPs). It covers the definition of LCs, classification, mesophase types and structures etc. The characteristic features of both conventional and non-conventional LCs along with their significance in both fundamental research and applied science have been discussed. A variety of experimental techniques used for the mesophase characterization have been presented. Several important applications of liquid crystals have been briefly presented in the concluding section of LCs. In the concluding section, the classification, synthesis and application aspects of COPs have been discussed briefly

Chapter II: Synthesis and characterization of three-ring chiralrod-like LCs

This Chapter deals with the synthesis and characterization of six different series (I-VI) of new chiral (optically active), three-ring rod-like LCs that have been structurally designed to stabilize the technically significant chiral smectic C (SmC*) phase. They are three-ring salicylaldimines (o-hydroxy Schiff bases) substituted on each terminal with a chiral tail (as a fixed segment) and an *n*-alkyl of varying length. The first two series of calmitics consist of (*S*)-2-octyloxy / (*R*)-2-octyloxy chains while the other four series have been derived from either (3*S*)-3,7-dimethyoctyl-6-enyloxy/(3*R*)-3,7-dimethyoctyl-6-enyloxy tails or (3*S*)-3,7-dimethyo-ctyloxy / (3*R*)-3,7-dimethyoctyloxy chains.

II.1. Ferroelectric three-ring chiral calamitics: Structure-property correlations

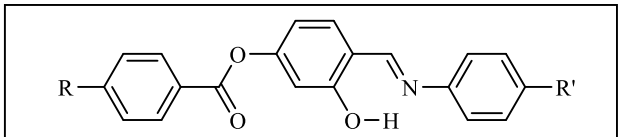
This portion portrays the relationship between the molecular structure of three-ring rod-like (calamitic) mesogens and the stabilization of the chiral smectic C (SmC*) phase.

II.2. Three-ring rod-like mesogens comprising chiral 2-octyloxy chains

This section described the synthesis and mesomorphism of five enantiomeric pairs of three-ring salicylaldimine mesogens(Series-I to II) comprising (*S*)-2-octyloxy and (*R*)-2-octyloxy chiral tails. The rational molecular design and synthesis of new rod-like LCs competent in displaying the SmC* phase by LC chemist is ongoing.[38-40]Such studies have been undertaken rigourously because most of the chiral mesogens synthesized to meet the target described above may not show the expected mesomorphism. Even if they show the SmC* phase, the other technical parameters required for their usage as either a single component system or chiral additive (dopant) to the host SmC phase to develop an FLC device may not suffice. It is well known that the mesogens under consideration should stabilize the ferroelectric SmC* phase over a wide thermal range existing between well-above and below the room temperature for the display device application. Importantly, it should possess high P_S value. It has been shown that the magnitude of P_S depends on the molecular tilt angle and the dipole of the chiral center.[38-40] The P_s value reduces if the rotations of the chiral center, besides other intra-molecular rotations,

are high around the long molecular axis of mesogens. In essence, the coupling among the dipole at the chiral centre and lateral dipole of the molecule is important in determining the magnitude of P_s value. The literature survey suggests that three-ring mesogens support the formation of the ferroelectric SmC* phase over an extended thermal range and provide an opportunity to modulate the P_s value. We have been working on this topic involving the molecular architecturing and synthesis of new three-ring chiral calamitics to realize FLCs for the possible usage in display fabrication. Recently, we have synthesized several enantiomeric pairs of three-ring Sciff bases and salicylaldimines where (*S*)-2-octyloxy and (*R*)-2-octyloxy chiral tails have been incorporated to account for the hindered rotation of a chiral moiety with respect to the aromatic core.[40a,b] The linking groups such as imine (-CH=N-) and ester (-COO-) linking groups have also been included in the structure to address the concern of inducing lateral polarity. These mesogens showed the ferroelectric SmC* phase over the temperature range of about 50−70°; remarkably, the P_s value was found to be over 100 nC/cm^2. However, the thermal stability of the FLCs derived from the salicylaldimine core was found to be high, as expected. Thus, we became interested in accomplishing analogous salicylaldimines comprising an *n*-alkyl (aliphatic) chain attached to the terminus of a rigid rod-like core.

Hence, two series of three-ring rod-like LCs (Series I-II), i.e. five pairs of enatiomers, have been synthesized and their general molecular structure has been shown below. Seemingly, each pair of enantiomers comprises (*R*)-2-octyloxy and (*S*)-2-octyloxy terminal chains; the length of the achiral, *n*-alkyl chain present at the other end has been varied to understand the structure-property relationships. These two series of mesogens have been referred to as **ASA(*R*)-n** (Series-I) and **ASA(*S*)-n**(Series-II), where **A,SA** and **n** denote alkyl, salicylaldimine and number of carbon atoms in the *n*-alkyl terminal tail; **(*S*)** and **(*R*)** specify the absolute configuration of chiral tail. The molecular structures of these new compounds have been determined with the help of both microanalytical and spectroscopic characterization data.



Series-I: **ASA(*R*)-n**	Series-II: **ASA(*S*)-n**
R = (*R*)-octyloxy	R = (*S*)-octyloxy
ASA(*R*)-4: R' = C_4H_9	**ASA(*S*)-4**: R' = C_4H_9
ASA(*R*)-5: R' = C_5H_{11}	**ASA(*S*)-5**: R' = C_5H_{11}
ASA(*R*)-6: R' = C_6H_{13}	**ASA(*S*)-6**: R' = C_6H_{13}
ASA(*R*)-7: R' = C_7H_{15}	**ASA(*S*)-7**: R' = C_7H_{15}
ASA(*R*)-8: R' = C_8H_{17}	**ASA(*S*)-8**: R' = C_8H_{17}

The examination of thermal behaviour with the help of several complementary techniques, viz., polarizing microscopy, differential scanning calorimetry, X-ray diffraction (XRD), shows that these five pairs of enantiomers display LC phases such as BP-I/II, N* and SmC* phases. As expected, the LC behaviour of a pair of enantiomers was found to be interchangeable. However, the length of the terminal tail dictates the LC property of these mesogens. The first two enantiomeric pairs (four compounds) comprising *n*-butyl and *n*-pentyl chains show enantiotropic N* phase in addition to the BP-I/II. The subsequent pair of enantiomers (two mesogens) derived from *n*-hexyl tail exhibit a monotropic SmC* phase in addition to the BP-I/II and N* phases. Notably, in the succeeding two pairs of enantiomers (four mesogens), the N* and SmC* exist enantiotropically, besides BP-I/II. It is immediately apparent that the long *n*-alkyl chains are essential for realizing the thermodynamically stable SmC* phase.

The SmC* phase of the compounds was subjected to electrical switching characteristics. The study confirmed that the switching property of these compounds is extremely poor, and thus, the P_s measurements were ruled out. The poor electrical response of these mesogens can be ascribed to the weak coupling between the asymmetric carbon atoms and the permanent dipole. In these mesogenic molecules, the lateral molecular dipole moment is quite low and their intramolecular rotations are not hindered. Furthermore, the samples possess ionic impurities, which also interrupted the ferroelectric switching measurements. Although ionic impurities were removed to whatever extent possible, the response of the samples was found to be infinitely low.

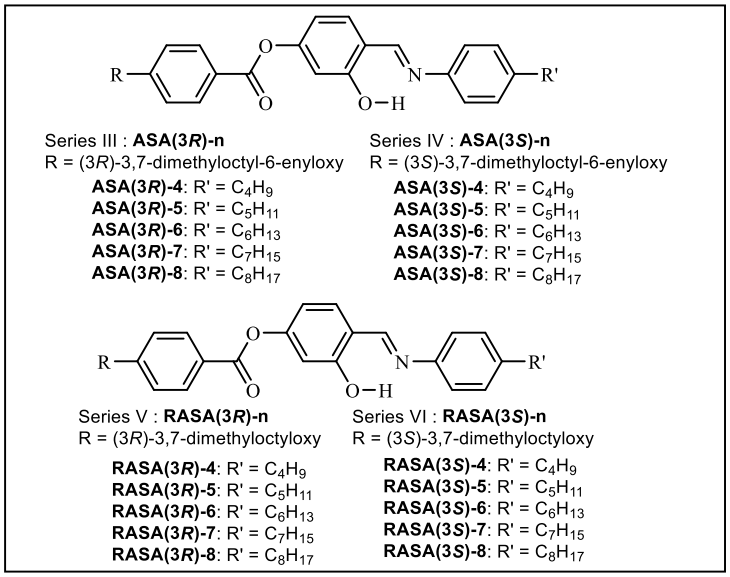
Fact that these compounds comprise chromophores, they were examined for their UV–Vis absorption and fluorescence (photophysical) properties. Especially, the UV–Vis absorption and fluorescence characteristics of these compounds have been studied in their solutions andthe condensed (solid) state. The Stokes shift in solution and in the solid-state of the materials was

found to be in the range of 171-179 nm, which is remarkable as such shifts avert the self-absorption or the inner filter effect. The chiroptical behaviourof the N* phase formed by a pair of enantiomers has been investigated by the circular dichroism (CD) spectroscopic method; as expected, they showed the mirror-image CD signals.

II.3: Three-ring calamitics having chiral 3,7-dimethyoctyl-6-enyloxy or 3,7-dimethyloctyl-oxy tails

In this second section of the Chapter, the molecular design, synthesis and liquid crystallinity of twenty new chiral three-ring rod-like LCs (Series-III to VI) terminally substituted with either (3*R*)-3,7-dimethyoctyl-6-enyloxy and (3*S*)-3,7-dimethyoctyl-6-enyloxy tails or (3*R*)-3,7-dimethyoctyloxy and (3*S*)-3,7-dimethyoctyloxy chains have been presented. As many as twenty new compounds (ten enantiomeric pairs) derived from salicylaldimine core have been prepared. As mentioned above, the value (magnitude) of the P_S reduces if the bond rotation of chiral centre around the long molecular axis of LC molecules is high. To substantiate this finding, we synthesized and investigated the LC property of twenty chiral three-ring rod-like LCs, which are either Schiff bases or salicylaldimines, comprising (3*S*)-3,7-dimethyloctyloxy and(3*R*)-3,7-dimethyloctyloxy tails.[40c] These compounds were found to show thermodynamically stable, chiral smectic C (SmC*) and chiral nematic (N*) phases besides blue phase-I/II (BPI or BPII). Notably, the SmC* phase persists over the temperature span of ~ 80-115 ^{o}C; notably, the SmC* phase displayed the ferroelectric switching with P_S in the range of 69-96 nC/cm^2. These observations prompted us to investigate analogous mesogens by replacing the *n*-alkoxy tails with the *n*-alkyl tail of the parent FLCs.[40c] The literature review indicates that the investigations on the SmC* phase stabilized by the mesogens comprising alkoxy tail bearing double bond(s) are rare. In other words, to the best of our knowledge, three-ring chiral rod-like LCs possessing a double bond in the terminal chiral tail have not been investigated for their mesomorphism. For these reasons, we intended to realize three-ring chiral salicylaldimines comprising either *n*-alkyl tail or simple (straight-chain) alkene tail at one of the ends of the central rigid core. Accordingly, we synthesized and characterized three-ring salicylaldimines comprising either (3*R*)-3,7-dimethyoctyl-6-enyloxy and (3*S*)-3,7-dimethyoctyl-6-enyloxy tails or (3*R*)-3,7-

dimethyloctyloxy and (3*S*)-3,7-dimethyoctyloxy. The general molecular structure of these four series of compounds has been shown below. For convenience, we denote Series-III, Series-IV, Series-V and Series-VI by the mnemonics **ASA(3*R*)-n**, **ASA(3*S*)-n**, **RASA(3*R*)-n** and **RASA(3*S*)-n**. Here, **A**, **SA** and **R** denote alkyl, salicylaldimine and reduced respectively and **n** indicates the number of carbon atoms in the *n*-alkyl terminal chain; **(*S*)** and **(*R*)** indicate the absolute configuration of chiral tail. The molecular structures of these newly synthesized mesogens have been ascertained by using data derived from both elemental analyses and spectroscopy.



The phase transitional behavior of these mesogens was ascertained with the aid of POM textural studies and DSC thermograms recorded during the first heating-cooling cycles at a rate of 5 ^{o}C / min. XRD measurements have been performed for some representative samples to confirm the mesophase structures. As expected, the individual pairs of enantiomers displayed an identical thermal behaviour. All the mesogens belonging to Series-III (**ASA(3*R*)-n**) and Series-IV (**ASA(3*S*)-n**), were found to be liquid crystalline exhibiting thermodynamically stable chiral smectic C (SmC*) LC phase besides chiral nematic (N*) phase and blue phase-I/II (BPI or BPII). Precisely, unlike other four enantiomeric pairs, the first pair of enantiomers havingthe *n*-butyl terminal tail exhibit metastable BP-I/II, N* and SmC* phases. Notably, all the five pairs of enantiomers (ten compounds) belonging to Series-V(**RASA(3*R*)-n**) and Series-VI(**RASA(3*S*)-n**), display an identical LC behaviour. They display SmC* and N* phases in addition to the BP-I/II. The representative mesogens chosen from each series were subjected to XRD measurements

to confirm the structure of the SmC* phase. In these series of compounds, the length of the terminal tail appears to influence the isotropization temperature; the clearing temperature seems to decrease with the increase in the terminal tail length. It is also noticeable that the thermal range/stability of the SmC* phase enhances with the increase in the length of the terminal tail.

Several representative mesogens chosen from each serieswere examined for their electrical switching property. The study clearly revealed that the mesogens probed respond feebly to the applied electrical field, and thus, the determination of P_s was excluded altogether. As mentioned earlier, the inadequate response of these compounds can be attributed to the weak coupling among the permanent dipole and asymmetric carbon atoms. The lateral molecular dipole moment is relatively small, and intramolecular rotations have not been restricted in these mesogens.

The SmC* and N* phases of several representative mesogens (enantiomers) were probed for their chiroptical property, mainly to figure out the helical twist sense, with the help of circular dichroism (CD) spectroscopic technique. The spectra recorded as a function of temperature clearly revealed the CD activity of these mesophases. Mirror imaging CD signals were observed in the CD spectra of the SmC* and the N* phases formed by a pair of enantiomers, as anticipated. The reversal of helical twist sense (handedness) from left to right and vice-versa was observed when phase transition from the N* phase to the SmC* occurs, suggesting that the helical twist sense of these two helicoidal structures of an enantiomer is opposite. Due to the occurrence of multiple chromophores and extended π-conjugations, these rod-like mesogens are expected to exhibit promising photophysical properties. Thus, the optical absorption (UV-Vis absorption) and fluorescence (photoluminescence) characteristics of these twenty compounds were studied in the solution and the solid-state. The photophysical study shows that these compounds have promising light-absorbing and emitting abilities.

Chapter III: Cholesterol-based nonsymmetric dimers: Synthesis and characterization

This Chapter portrays the preparation and characterization of eight series of nonsymmetric dimers derived from cholesterol. They are formed by covalently linking cholesterol with a three-ring mesogenic core through a flexible spacer. The recent findings that

cholesterol unit linked to either three-ring or four-ring mesogenic cores favour the unique LC phase sequences and frustrated LC phases inspired us to undertake the current study.The mesogenic dimers of Series-I to IV comprise an achiral three-ring salicylaldimine core and cholesterol unit interlinked via an ω-oxyalkanoyloxy spacer of varying length and parity. The length of the terminal tail attached to the salicylaldimine core has been varied to understand the relationship between the molecular structure and liquid crystallinity. In compounds belonging to Series-V to VIII, a chiral three-ring salicylaldimine mesogenic core has been tied covalently to cholesterol via an ω-oxyalkanoyloxy spacer of varying length and parity. In particular, three-ring salicylaldimine core has been terminally substituted with either (*R*)-2-octyloxy and (*S*)-2-octyloxy or (3*S*)-3,7-dimethyloctyloxy and (3*R*)-3,7-dimethyloctyloxy tails terminal chains.

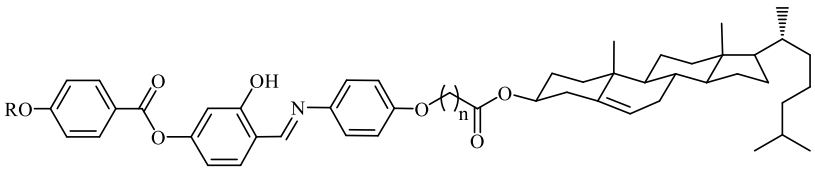
III.1. Cholesterol-based liquid crystal dimers: An overview

This part of the thesis deals with the LC dimers derived from cholesterol. It mainly portrays the molecular structural aspects, and the typical LC behaviour of the dimers. The relationship between molecular structure and LC properties has also been covered briefly.

III.1. Cholesterol-based liquid crystal dimers comprising three-ring salicylaldimine core

The synthesis, molecular structural characterization, mesomorphism, chiroptical behaviour and photophysical properties of twenty new nonsymmetric dimers belonging to Series-V to Series-VIII have been described in this section. As indicated earlier, the dimers resulting from the combination of cholesterol and long (rigid) mesogenic core display short pitch cholesteric phase and thus, frustrated phases such as twist grain boundary (TGB) phases and blue phases (BPs).[41,86]Besides, they not only stabilize technically significant mesophases such as SmC* and SmA phases but also displaynew/unusual phase sequences. Inspired by these findings, we became interested in realizing cholesterol-based dimers comprising three-ring (long-rigid) core. Thus, we have synthesized and characterized nonsymmetric LC dimers made by covalently linking a three-ring core namely, 3-hydroxy-4-((phenylimino)methyl)phenyl benzoate (salicylaldimine) core to a cholesterol unit via an ω-oxyalkanoyloxy spacer.In particular, four series of dimers have been realized by incorporating three even-membered spacers, namely 4-

oxybutanoyloxy, 6-oxyhexanoyloxy and 8-oxyoctanoyloxy, and an odd-parity spacers viz., 5-oxypentanoyloxy spacer. In each series, the length of the central spacer is fixed whereas the length of the terminal tail attached to the salicylaldimine core has been varied. That is, the three-ring core is terminally substituted with *n*-hexyloxy, n-heptyloxy, n-octyloxy, *n*-decyloxy and*n*-dodecyloxy chains. The general molecular structure of these twenty LC dimers synthesized has been presented below. The abbreviation **CSAD-n,m** has been used for the



CSAD-n,m series, R = C_mH_{2m+1}; n = 3, 4, 5 & 7; m = 6, 7, 8, 10 and 12

Series-I : **CSAD-3,m**
CSAD-3,6; R=C_6H_{13}
CSAD-3,7; R=C_7H_{15}
CSAD-3,8; R=C_8H_{17}
CSAD-3,10; R=$C_{10}H_{21}$
CSAD-3,12; R=$C_{12}H_{25}$

Series-II : **CSAD-4,m**
CSAD-4,6; R=C_6H_{13}
CSAD-4,7; R=C_7H_{15}
CSAD-4,8; R=C_8H_{17}
CSAD-4,10; R=$C_{10}H_{21}$
CSAD-4,12; R=$C_{12}H_{25}$

Series-III : **CSAD-5,m**
CSAD-5,6; R=C_6H_{13}
CSAD-5,7; R=C_7H_{15}
CSAD-5,8; R=C_8H_{17}
CSAD-5,10; R=$C_{10}H_{21}$
CSAD-5,12; R=$C_{12}H_{25}$

Series-IV : **CSAD-7,m**
CSAD-7,6; R=C_6H_{13}
CSAD-7,7; R=C_7H_{15}
CSAD-7,8; R=C_8H_{17}
CSAD-7,10; R=$C_{10}H_{21}$
CSAD-7,12; R=$C_{12}H_{25}$

general description of these four series of dimers; here, **C, SA,** and **D** respectively signify cholesterol, salicylaldimine and dimer. The acronyms **n** and **m** denote the number of carbon atoms in the terminal alkyl chain and the number of methylene units in the spacer respectively. The four series of dimers derived each from the spacer namely, 4-oxybutanoyloxy, 5-oxypentanoyloxy (C_5), 6-oxyhexanoyloxy, and 8-oxyoctanoyloxy have been accordingly denoted by mnemonics **CSAD-3,*m***, **CSAD-4,*m***, **CSAD-5,*m*** and **CSAD-7,*m***.

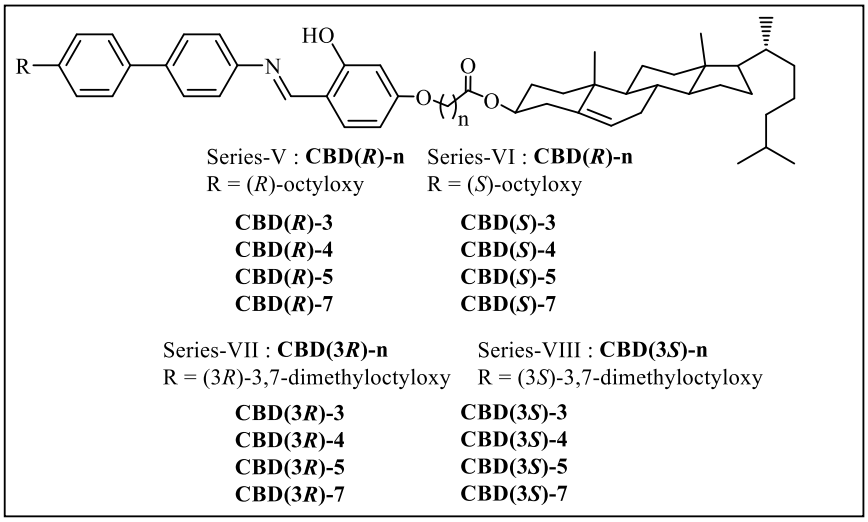
The phase transitional property of the dimers synthesized has been probed with the complementary techniques such as POM, DSC and X-ray diffraction. In general, all the twenty compounds exhibit thermodynamically stable mesophases which included BP-I/II, N* and TGBC* phases. It is very well known that the LC dimers with an even-numbered spacer behave differently from their odd-membered counterparts, which is called odd-even effect. Such a behaviour, which persists in these four series of compounds, has been characteristically ascribed to the bent-conformation and the rod-like shape attained by the odd-membered and even-

membered dimers respectively. Interestingly, the first member of all the series bearing n-hexyl tail, irrespective of the length and parity of the spacer, show the N* phase solely whereas rest of the dimers show multiple mesophases. The dimers comprising an even-parity spacer and *n*-heptyloxy, *n*-octyloxy, *n*-decyloxy and *n*-dodecyloxy terminal tails display thermodynamically stable N* and TGBC* phases. The TGBC* phase over wide thermal range (60 -170 ^{o}C), which is remarkable given the fact that it is a highly frustration and complex LC structure. The length of the central spacer appears to influence the thermal width of the TGBC* phase. The thermal range of the phase decreases with increase in the length of the spacer. On the other hand, the dimers with odd-parity show different behaviour as expected. Generally, they display BP-I/II and N* phases, and the dimers with *n*-octyloxy, *n*-decyloxy and *n*-dodecyloxy tails stabilize an unknown chiral smectic (SmX*) phase additionally. The structure of the TGBC* phase has been evidenced with the help of XRD data recorded as a function of temperature for some representative samples. Photophysical measurements, in the solution and solid state, have been carried out to demonstrate light absorption and photoluminescence characteristics of the LC dimers synthesized. CD spectra of the N* phase have been recorded as a function of temperature for four representative samples chosen each from four series.

III.2. Cholesterol-based dimers comprising three-ring salicylaldimine core derived from biphenyl

In this section, the preparation, molecular structural confirmation, liquid crystallinity chiroptical properties and photophysical behaviour of sixteen new (eight enantiomeric pairs) of nonsymmetric dimers belonging to Series-V to Series-VIII have been portrayed. They comprise a three-ring chiral salicylaldimine core and cholesterol unit interlinked through a ω-oxyalkanoyloxy spacer of varying length and parity. The chiral tails namely, (*R*)-2-octyloxy and (*S*)-2-octyloxy / (3*S*)-3,7-dimethyloctyloxy and (3*R*)-3,7-dimethyloctyloxy tails have been used as terminal substituents of the three-ring mesogenic core derived from the biphenyl core. We were prompted to realize such dimers for the several valid reasons and findings. As mentioned earlier, the incorporation of long, rigid mesogenic core in the molecular architecture of cholesterol-based dimers generally leads to interesting LC behaviour involving the stabilization of unique phase sequences, re-entrant phases, and frustrated fluid phases. Thus, to account for

the rigidity we conceived an idea of incorporating the biphenyl core in three-ring salicylaldimine core. On the other hand, it is well demonstrated that the incorporation of chiral tails such as (*R*)-2-octyloxy and (*S*)-2-octyloxy units not only serve purpose of inducing molecular chirality but also aids in enhancing the magnitude of polarization due to hindered rotation of the chiral moiety. Likewise, the insertion of (3*S*)-3,7-dimethyloctyloxy /(3*R*)-3,7-dimethyloctyloxy tails also have advantages in the molecular design of the LCs; the lowering of the transition temperature is very attractive feature of these chiral tails apart for inducing molecular chirality. The general molecular structure representing all the eight pairs of cholesterol-based dimers is shown below. The acronyms used for these dimers are **CBD(*R*)-n**, **CBD(*S*)-n**, **CBD(3*R*)-n** and **CBD(3*S*)-n** where **C** stands for chiral, **B** stands for biphenyl and **D** stands for dimer; n signifies the number of methylene units of the spacer and **(*S*)&(*R*)** indicate the absolute configuration of the chiral tail.



The liquid crystal properties were studied using an optical polarizing microscope. The thermal data of the phase transitions were derived from DSC traces. In general, the LC behaviour of a pair of enantiomers under consideration were found to be exactly matching as expected. All the sixteen chiral dimmers synthesized were found to be liquid crystalline and exhibiting a rich mesomorphism. The dimers derived from (*R*)-2-octyloxy and (*S*)-2-octyloxy showed the mesophases such as BP-I/II, N*, TGB, SmA and SmC* phases; the dimers having longer spacer replace the SmC* phase other highly ordered smectic (SmX_1 and SmX_2) phases. Interestingly, a similar phase transitional behaviour was witnessed for the dimers comprising (3*S*)-3,7-dimethyloctyloxy /(3*R*)-3,7-dimethyloctyloxy tails meaning that the change in the

chemical nature of the chiral tails has no effect on the mesomorphism. Although the parity of the spacers in these series viz., **CBD(*R*)-n**, **CBD(*S*)-n**, **CBD(3*R*)-n** and **CBD(3*S*)-n**, did not affect the overall phase sequences, the odd-even effect was noticed on the clearing temperatures of the dimers. In view of the fact that these dimers comprise multiple chromophores, they were examined for their photophysical behaviour. The excitation and photoluminescence spectra of the synthesized dimers were recorded in dilute solutions as well as in condensed (solid) state. The CD spectra recorded as a function of temperature in the entire thermal width of the N* phase stabilized by the enantiomeric pairs exhibit excellent mirror-image relationships, as expected.

Chapter IV: Phasmidic bis(*N*-salicylideneaniline) mesogens: Synthesis and characterization

This Chapter describes the synthesis, characterization, and Excited-State Intramolecular Proton-Transfer (ESIPT) activity of a homologous series of novel phasmidic bis(*N*-salicylideneaniline) columnar (Col) liquid crystals (LCs). ESIPT Col liquid crystals have been projected as the apt materials for advanced technological endeavours. However, there are hardly any explorations in this direction and thus, needing immediate attention. In view of this, a series of novel hexacatenar bis(*N*-salicylideneaniline) LCs have realized.

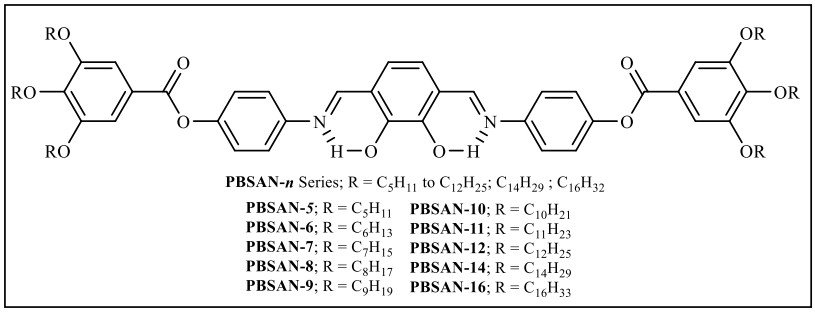
IV.1. Phasmidic (hexacatenar) liquid crystals: An overview

In this portion of thesis, a brief account of phasmidic or polycatenar LCs has been given. It covers the basic aspects of these non-discoid LCs, their discovery, classification, mesophase types, etc. The distinguishing features of different polycatenary LCs are discussed. The significance of a wide variety of functional phasmids reported has been discussed.

IV.2. Molecular design, synthesis and characterization of hexacatenar bis(*N*-salicylidene-aniline) mesogens:

As mentioned earlier, phasmidic or polycatenar mesogens possess a long rod-like rigid core ending on either side with lipophilic entities having two or three flexible tails. [45-60] They have been categorized depending upon the total number of *n*-alkoxy tails they comprise.

Polycatenars having four, five and six terminal paraffinic chains have been respectively referred to as tetracatenars, pentacatenars and hexacatenars. In fact, they bridge the gap between conventional calamitic and discotics LCs.[45-60] The hexacatenars (phasmids) have been the topic of many researchers because of their inherent ability to self-assemble into Col phase. Importantly, they provide the prospect of inserting functional features via the choice of predetermined molecular structural segments. Because of their technological significance, the light emitting phasmidic LCs have been attracting a great deal of attention.[63-79]However, there are hardly any investigations focussing on ESIPT Col LCs derived from the fluorescent mesogens. Thus, we perceived the idea of realizing novel fluorescent hexacatenar columnar LCs capable of displaying the ESIPT activity. Of the various types of ESIPT active molecules reported hitherto, [86] salicylideneanilines attracted our attention owing to their potential for various technological endeavors. [59] In particular, the investigations on phasmidic LCs by Hiremath [59b,c] clearly hinted that the mesomoprism can be induced in bis(*N*-salicylideneaniline)s (BSANs).That is, these compounds have the intrinsic ability to display ESIPT fluorescence owing to their novel structural composition where the intramolecular hydrogen (H)-bonding correlation among a hydrogen bond donor (–OH) group and a hydrogen bond acceptor (-C=N, imine) linking group exists. Despite these exciting features, the studies on the photophysical properties of such LCs have not been revealed hitherto. Thus, we set out our goal to realize the analogs of BSAN hexacatenars and evaluate their ESIPT activity. Accordingly, ten new ESIPT active phasmidic bis(*N*-salicylideneaniline)s(**PBSANs**) have synthesized and characterized. The molecular structure of these newly synthesized **PBSANs** is shown below.



PBSAN-*n* Series; R = C_5H_{11} to $C_{12}H_{25}$; $C_{14}H_{29}$; $C_{16}H_{32}$

PBSAN-*5*; R = C_5H_{11} **PBSAN-10**; R = $C_{10}H_{21}$
PBSAN-6; R = C_6H_{13} **PBSAN-11**; R = $C_{11}H_{23}$
PBSAN-7; R = C_7H_{15} **PBSAN-12**; R = $C_{12}H_{25}$
PBSAN-8; R = C_8H_{17} **PBSAN-14**; R = $C_{14}H_{29}$
PBSAN-9; R = C_9H_{19} **PBSAN-16**; R = $C_{16}H_{33}$

The thermal properties of the newly synthesized compounds have ascertained with the help of POM, DSC and X-ray diffraction studies. The optical textural patterns combined with XRD data analysis confirm the presence of Col_h having *p*6*mm* symmetry. XRD results imply that the slices (disk-like columnar core), formed by the self-assembly of two molecules in a side-to-

side fashion, tilt with respect to the columnar axis and tilt direction among the columns is not correlated; the profiles also show that the core-core (slice-to-slice) interactions are too weak. Photophysical measurements clearly revealed the intrinsic ESIPT phenomenon not only in their dilute solutions but also in their solid, liquid crystal (Col) phase and isotropic liquid state. In the Col_h phase, the magnitude of ESIPT fluorescence emission intensity display temperature-dependence; the emission maxima shift to longer wavelengths upon decreasing the temperature confirming the J-type aggregation in the mesophase. Electron distribution in the optimized structures and band-gaps of the HOMO and LUMO for the enol and keto states determined by HF and DFT-based calculations support the photophysical experimental observations. The evaluation of metal ions chelating property reveals that a mesogen (as a representative case) selectively binds to certain metal ions to form metal complexes; notably, the complex formation of mesogen with Zn^{2+} ions not only enhance the emission intensity but also shifts the peak towards shorter wavelength. The electrochemical band gap values determined from the CV experiments appear to match with those derived from the theoretical calculations closely. In essence, these phasmidic columnar LCs exhibiting ESIPT phenomenon and other physicochemical properties may serve as functional materials for various technological applications.

Chapter V: Preparation, structural characterization and sensing properties of coordination polymers

This Chapter deals with the preparation, characterization and explosive sensing abilities of five new, fluorescent coordination polymers **(**COPs) derived from lanthanide. They have been realized by treating a tetraamine namely viz., 3,3'-diaminobenzidine (DAB) with lanthanide salts namely, praseodymium(III) acetate hydrate - $Pr(OAc)_3.xH_2O$, neodymium acetate hydrate - $Nd(OAc)_3 \cdot xH_2O$, samarium(III) nitrate hexahydrate - $Sm(NO_3)_3 \cdot 6H_2O$, europium(III) acetate hydrate - $Eu(OAc)_3 \cdot xH2O$ and gadolinium(III) nitrate hexahydrate - $Gd(NO_3)_3.6H_2O$. The detailed study in respect their structural elucidation and their ability to sense the high energy materials (HEMs) (explosives) have been presented.

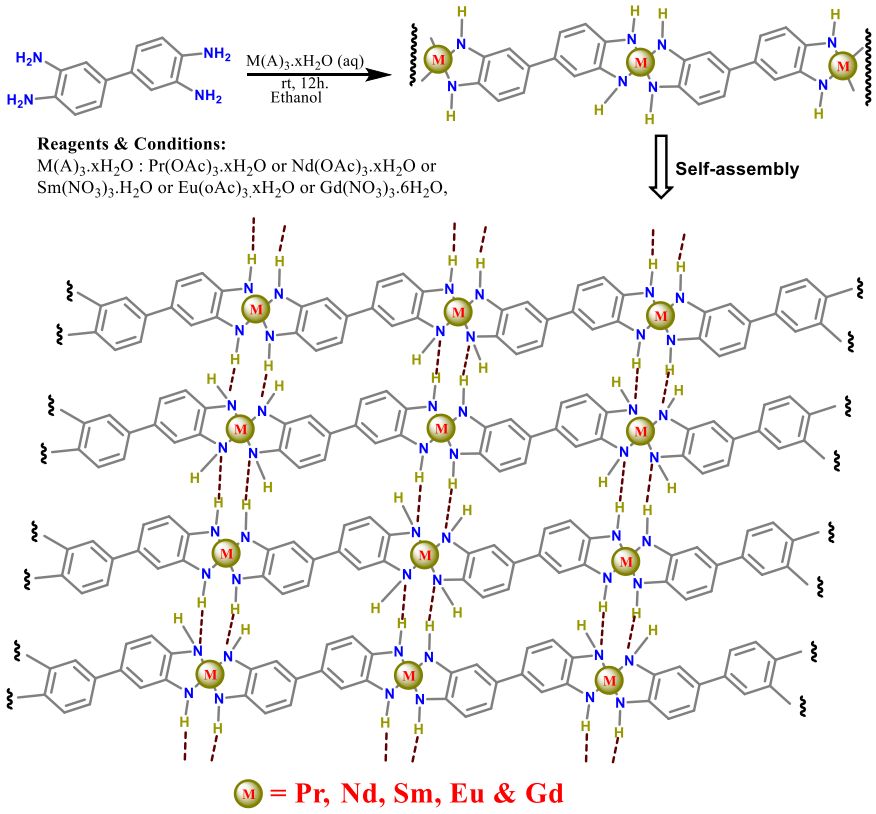
V.1. Coordination polymers: An overview

This section of the thesis deals with the various aspects of coordination polymers (COPs) and thereby, it makes acquainted the readers to the filed. It covers the definition, molecular structure, classification, and various distinguishing properties of COPs. The correlation between the molecular structure (involving different ligands and metal ions) and functional properties has also been discussed in this portion.

V.2. Fluorescent COPs for explosive detections

The preparation and characterization of five new fluorescent COPs and their inherent ability to serve as "turn-off" photoluminescent sensors toward explosives have been presented in this section. Explosives, which are basically the high energy materials (HEMs), being hazardous substances pose big threats to national/international security and civil society. Moreover, they inflict multi-organ lethal wounds and contaminate/harm the atmosphere. Hence, the on-field, ultra-fast sensing/detection of HEMs has become a very important and challenging task for scientists and technologists. [33-37] Unceasing efforts have been made all over the world to develop new and innovative techniques or improve the existing methods or sensors (devices). [24,33-37] Among all, the luminescence technique/method of sensing HEMs appears to be feasible and effective. In this method, needless to say, the intensity of light emitted by sensor (chemosensor) gets quenched (reduced) considerably that can be visualized and quantified effortlessly. However, such sensors have several issues such as chemical/thermal stability, sensitivity/accuracy, selectivity, detection limit, cost of production etc. Currently, the luminescent COPs and MOFs have been attracting a considerable attention because of their ability to serve as active media for many devices. Thus, there have been efforts utilize them for sensing the presence of HEMs. [24,28-32]However, it appears that COPs have not been explored in this direction to their true potential. [24, 28-32]We were therefore inspired to design and realize new COPs that have the ability address all the concerns mentioned above. We chose to incorporate trivalent lanthanide ions owing to their unusual but promising electronic properties; they can be

regarded as the luminescent indicators that have many developing applications at present. Most importantly, visible light emitting lanthanides have a distinctive luminescence colour allowing for easy usage in sensing phenomenon. Thus, we have realized five novel, luminescent COPs by treating 3,3'-diaminobenzidine (DAB) with lanthanide salts (hydrated) such as $Pr(OAc)_3$, $Nd(OAc)_3$, $Sm(NO_3)_3$, $Eu(OAc)_3$ and $Gd(NO_3)_3$, as shown below; they possess 2D structure resulting from the self-assembly of COP strands. For the sake of convenience they have been denoted by mnemonics **Pr(DAB)**,**Nd(DAB)**,**Sm(DAB)**,**Eu(DAB)** and **Gd(DAB)**.



The molecular structures of these complexes have been ascertained using characterization data collected from both spectroscopic and elemental analyses. Photophysical measurements were carried out for the millimolar (mM) solutions of COPs at room temperature to validate their light absorption and photoluminescence features. To examine the sensing abilities, all the five COPs in the form of their dilute solution were titrated with different explosives such as ammonium nitrate (AN),2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL20), pentaerythritol tetranitrate (PETN), 2,4,6-trinitrophenol(TNP), 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The experimental /measurement results evidence the HEM sensing

abilities of the prepared lanthanide COPs. That is, results obtained from Stern-Volmer (S-V) plots indicates picric acid (PA) have highest quenching efficiency among all the HEMs quenchers used. The S-V plot also provide information about the quenching efficiency of COPs with different quenchers. The quenching constant obtained clearly indicates that the Pr(DAB) has highest quenching efficiency with TNP in comparison with other COPs. This was further supported by the data obtained from Benesi-Hildebrand (B-H) plots using picric acid for different COPs. The highest binding constant for Pr(DAB) indicates its stronger affinity to interact with TNP which subsequently quenches its fluorescence.

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